Mini review

Magnetic fields in electrochemistry: The Kelvin force. A mini-review

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Recent work on the influence of magnetic field gradients on paramagnetic species in an electrochemical cell is reviewed. The effects include normal patterning and inverse patterning of electrodeposits, stabilization of paramagnetic liquid structures and enhanced rates of reactions involving the magnetic species.

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1. Introduction

Much early work in magnetoelectrochemistry was devoted to a study of the effect of the Lorentz force on convection on the scale of the electrochemical cell. Magnetohydrodynamic effects involving the interaction of the field with the local electric current density are the topic of a short companion review [1]. Here we focus on to the forces acting directly on paramagnetic species in the electrolyte. Interest in the effects of magnetic field gradients on the moments of paramagnetic free radicals in solution was stimulated by the work of White and co-workers [2,3]. The Kelvin forces associated with magnetic field gradients are ubiquitous because any redox process where a single

electron is transferred generally involves paramagnetic species. We consider how they can maintain or create local paramagnetic concentration gradients, and induce convection near an electrode.

2. Forces on paramagnetic species

The magnetic species in an electrolyte are usually paramagnetic cations, free radicals or molecular species with unpaired spin such as O_2. An applied field $\boldsymbol{H}$ induces a magnetization $\boldsymbol{M} = \chi \boldsymbol{H}$. The dimensionless Curie-law magnetic susceptibility of these species in aqueous solution is [4]

$$\chi = n\mu_0 g^2 \mu_B^2 J(J+1)/3k_B T \tag{1}$$

where n is the number per cubic meter, μ_0 is the magnetic constant $4\pi\,10^{-7}$ T mA^{-1}, μ_B is the Bohr magneton, J is an appropriate quantum

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number (spin for a 3d cation) and g is a constant between 1 and 2. H is related to B in free space by $H = B / \mu_0$. Paramagnetic susceptibilities are low at room temperature, ranging from $16 \cdot 10^{-6}$ for 1 M Cu^{2+} or free radicals (J = 1/2; g = 2) to $594 \cdot 10^{-6}$ for 1 M Dy^{3+} (J = 15/2; g = 4/3) at 300 K, so the magnetization of an electrolyte in an applied field is always very small compared to the field that induces it. For this reason, the difference between the fields B and $\mu_0 H$ can be safely ignored in electrochemistry. The three quantities are related by the equation

$$B = \mu_0(H + M) \qquad (2)$$

which can be regarded as the definition of the H-field that is responsible for inducing magnetization, in terms of the fundamental B-field and the magnetic moment M per unit volume of the electrolyte.[2]

An applied field $B = 1$ T ($H \approx 800$ kAm^{-1}) induces a room-temperature magnetization ranging from 13 Am^{-1} for Cu^{2+} to 475 Am^{-1} for Dy^{3+}. In atomic terms, the induced moments are only $2.2 \cdot 10^{-3}$ μ_B and $8.4 \cdot 10^{-2}$ μ_B per ion, respectively, which may be compared with their saturation values of 1 and 10 μ_B.

2.1. Uniform magnetic fields

Liquids have no inherent form. The shape of an inclusion of a paramagnetic solution in water or another pure solvent is normally determined by a balance of interface tension and gravity. As a result of the weak magnetization induced by a uniform field there is no net force, but a weak stress $\sigma_M = MB$ known as the *Maxwell stress* acts on the inclusion. This is able to deform the regions of liquid where paramagnetic ions are concentrated [5], and it is expected to influence the shape of ion clouds near an electrode surface, with possible consequences for the capacitance of the electrochemical double layer. Otherwise, a uniform magnetic field is not expected to influence the distribution of paramagnetic species when $\chi \ll 1$. In particular there is no 'concentration gradient' force of the form $(1/2 \mu_0) \chi_m B^2 \nabla c$ in a uniform field [6], where χ_m is the molar susceptibility and c is the concentration of magnetic species in mol m^{-3}. Unlike a ferrofluid, which is strongly magnetized by an applied field, the weakly-magnetized electrolyte is indifferent to its location in a uniform field.

2.2. Nonuniform magnetic fields

The situation is different when the magnetic field is non-uniform. The Zeeman energy of the paramagnetic species is $-(1/2 \mu_0)c\chi_m B^2$ now depends on position, so there is a force on the dissolved magnetic species which tends to draw it into regions where the magnitude of the field is greatest. The Kelvin force density (also known as the magnetic field-gradient force or magnetophoretic force) is given by the following formula:

$$F_K = (1/2\mu_0)c\chi_m \nabla B^2. \qquad (3)$$

The force (also denoted as $F_{\nabla B}$) is proportional to the paramagnetic susceptibility of the species in solution, the magnitude of the magnetic field and its gradient ($\nabla B^2 = 2(B \cdot \nabla)B$). With representative numbers, c = 1000 mol m^{-3} (1 M), $\chi_m = 10^{-8}$, B = 1.25 T, $\nabla B = 100$ Tm^{-1}, we find $F_K \sim 1000$ N m^{-3}, a value which will influence convection. Unlike the Lorentz force, $F_L = J \times B$, where scope for increase is limited

by the maximum current that can be safely driven through the electrolyte, the Kelvin force can be increased substantially by patterning ferromagnetic elements on a small enough scale to create a rapidly-varying magnetic stray field in the electrolyte. If this is done on a microscale, F_K may be as large as 10^6 or 10^7 N m^{-3}, although the forces are confined to tiny regions in the vicinity of the ferromagnetic elements. Nevertheless, field gradient forces are not normally expected to compete with thermally-driven diffusion, because the energy of a hydrated paramagnetic ion in the field is always far less than $k_B T$ at ambient temperature. Nor can they compete with electrostatic forces in the double layer. The electrostatic and magnetic gradient forces per ion are of the order pN and aN, respectively, a difference of six orders of magnitude.

Unlike the Lorentz force, which drives magnetohydrodynamic (MHD) convection via the electric current although the force itself is formally conservative ($\nabla \times F_L = 0$; since $\nabla \cdot B = \nabla \cdot j = 0$), the Kelvin force (3) is not conservative in the presence of a nonuniform distribution of paramagnetic species [$\nabla \times F_K = (1/2 \mu_0) \chi_m (\nabla c \times \nabla B^2)$], so it too can be expected to give rise to convection in the vicinity of an electrode where there is a paramagnetic concentration gradient [7,8]. The field gradient ∇B^2 and concentration gradient ∇c must be noncollinear for this vorticity to appear. When the field gradient is parallel to the electrode surface the resulting convection will thin the diffusion layer, and as with MHD due to F_L the current is enhanced.

Magnetic field gradients near the surface of the working electrode have been exploited to pattern electrodeposits. This has been done with a magnetized nickel grid [9], an array of magnetized iron wires [10] or an array of small permanent magnets [11,12]. The pattern obtained depends not only on the type of array – permanent magnets have the advantage that the field can be arranged to be mainly parallel or mainly perpendicular to the electrode by aligning alternating magnetic dipoles antiparallel or parallel to each other – but it is also governed by the magnetic properties of the ions in solution, as well as their redox potential. The effects can be separated into *direct* patterning and *inverse* patterning (Fig. 1).

Direct patterning is achieved when depositing a metal from a solution of paramagnetic ions, like Cu^{2+}, Ni^{2+} or Co^{2+} [9–13]. Thicker and rougher deposits are obtained on regions of the cathode where the field is concentrated, while the film is thinner everywhere else. The localized deposits can be separated by pulse-reverse plating to redissolve the thinner layers of metal [14]. The localized deposits become dendritic when the metal is ferromagnetic, locally focusing both electric and magnetic fields on a submicron scale [9]. Some electrodeposits obtained with an array of permanent magnets in a parallel or alternating configuration are shown in Fig. 1. The field created in the vicinity of the cathode is larger in the alternating configuration, and therefore its effect on modulating the diffusion layer is more intense
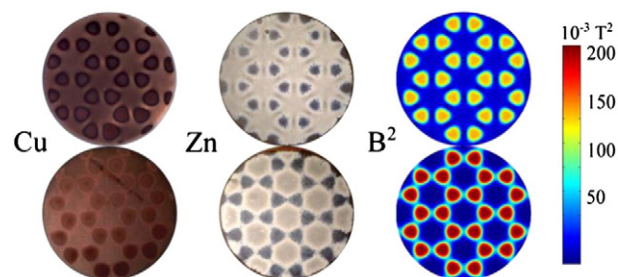

Fig. 1. Patterned electrodeposits on copper or silver cathodes above hexagonal arrays of 2 mm cylindrical magnets. In the top row, the magnets are all aligned parallel, whereas in the bottom row, the polarity is alternating. On the left are direct deposits of copper from $CuSO_4$ solution. In the middle are inverse deposits of diamagnetic zinc from a Zn^{2+}/Dy^{3+} solution. The calculated stray field pattern at the cathode is shown on the right [13]. Copyright (2012) American Physical Society, reprinted with permission.

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[2] Much research literature in magnetism is written in the old cgs system, where μ_0 is a dimensional constant numerically equal to 1. In that system $B = H + 4\pi M$, and $\chi = M / H$ is smaller by a factor 4π. The units of B and M are Gauss, and the units of H are Oersteds. 1 Oe $\approx$ 80 Am^{-1} and 1 G $= 10^{-4}$ T. The compelling advantages of the SI system used here are its dimensional transparency and compatibility with standard electrical units.